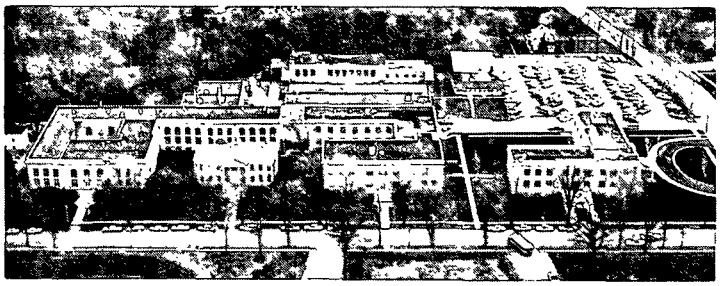

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EFFECT OF WOOD PREPARATION ON OXYGEN PULPING OF LOBLOLLY PINE

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INTRODUCTION

Oxygen pulping shows great promise for reducing the pollution associated with kraft and other pulping processes. Since sulfur is not used in this new process, odor problems are virtually eliminated. Although many difficulties remain to be completely solved, the process is on the verge of becoming a commercially important process.

One of the problems requiring solution is the mass transfer problem of getting oxygen to the site of reaction with lignin in the wood. One method is to expose more wood surface. This must be accomplished with a minimum amount of fiber damage. This manuscript, submitted to Tappi for publication, describes several methods of fiber preparation. These were characterized by several physical methods, and evaluated by oxygen pulping under conditions of high oxygen availability. The results show that sample preparation is an important parameter in oxygen pulping.

Effect of wood preparation on oxygen pulping of loblolly pine

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Abstract

Several forms of loblolly pine were compared as starting materials for oxygen pulping under oxygen-rich conditions. These included fiberized with sodium hydroxide, fiberized with sodium carbonate/bicarbonate, conventional chips, rolled chips, and thin flakes. The mechanical damage due to fiberization was characterized microscopically and found to be compressive. Strength comparisons among the various oxygen pulps showed the flakes and rolled chips gave the best strength. Kraft pulping was used to show that a substantial portion of the strength deficit compared to kraft was due to sample preparation.

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INTRODUCTION

Oxygen/alkali (OA) pulping offers several advantages over existing commercial chemical pulping methods. Higher yields are generally obtained, and the elimination of sulfur greatly simplifies odor and chemical recovery problems. If sodium carbonate and/or bicarbonate are used, wet combustion becomes an attractive alternative to more conventional recovery systems. Economic assessments, although incomplete, have not ruled out the process. The main problem impeding the commercialization of OA pulping on a large scale is the inferior strength properties of the pulps, when compared to kraft. This shows up most in softwood pulps, where strength is of paramount importance (1).

The low solubility of oxygen in pulping liquors at reaction temperatures leads to a severe mass transfer problem. Getting the oxygen to the lignin for reaction requires exposing as much wood surface to the liquor or gas phase as possible. This has generally been done by some type of mechanical treatment, often following an alkaline pretreatment which could be considered a separate cook. Much of the emphasis in the past has been on the OA pulping conditions, whereas a great deal of the strength loss can be attributed to the mechanical treatment.

This paper describes a number of pretreatments which were used with loblolly pine in an attempt to improve the strength properties of OA pulps prepared under conditions of high oxygen availability (1). Although significant differences in the strengths of the various pulps were observed, and some progress was made in approaching the properties of kraft, no combination was found which produces a pulp with strength equal to kraft.

PREPARATION OF STARTING MATERIALS

Fiberized Loblolly Pine

One approach to getting oxygen to the lignin in the wood is to separate the wood into fiber bundles. This can be done by fiberizing chips in a disk refiner. If this is done at temperatures above the softening point of lignin, using wide plate gaps, separation takes place between fibers, in the middle lamella, rather than through fiber fracturing.

A number of fiberizations were carried out under a variety of conditions. Two of these were used for the work reported here, and were labelled A-2 and A-3. The samples were impregnated at 10% consistency for 30 minutes at 90°C under 100 psi air pressure. Excess liquor was drained from the chips, leaving approximately 11% NaOH on A-2 and 2.4% Na_2CO_3 and 1.8% $NaHCO_3$ on A-3. These were then preheated to 160°C during ca. 4 minutes and fiberized at 37% consistency in a Bauer 418 pressurized double disk refiner with a plate gap of 0.025 inch. Power input was only 2-3 horsepower days/air-dry ton. This produced a coarse material consisting of fiber bundles, 65-82% of which was retained on 14 and 28 mesh screens in Bauer-McNett classifications. Fiber length distributions after gentle delignification with chlorite and peracetic acid were similar to a control sample which was not fiberized. Yields were simulated in the laboratory, since a material balance was impossible with the pilot plant equipment. An Asplund mill was used for preheating. The sample was discharged directly into an atmospheric Sprout-Waldron disk refiner. The simulated yields for A-2 and A-3 were 81.0 and 91.6%, respectively.

The materials were examined by scanning electron microscopy after the above-mentioned gentle delignification. Two different magnifications were used, and the micrographs are shown in Fig. 1. At 50X magnification, a general picture of the sample is obtained. Fiber bundles have been partially separated by the delignification, so the degree of aggregation is not meaningful. Sample A-2, which was fiberized in NaOH, appears more flexible than A-3. The fibers in A-2 also appear to be twisted more, although it is difficult to be sure that a representative sample was obtained. At 500X magnification, areas which showed specific types of damage were selected, and should not be considered representative of the samples as a whole. Some cracking, delamination, and ragged ends can be seen at this magnification. Fiberization, however, does appear to have been primarily in the middle lamella, between fibers, rather than within fibers, which is generally the case at the lower temperatures used in thermomechanical pulping. This process thus leaves the outer surfaces rich in lignin, and should aid delignification with oxygen/alkali.

Swelling with cupriethylenediamine (CUENE) was also used to characterize mechanical damage from fiberization. One drop of 20% CUENE solution was placed on a small sample of fibers which had been previously stained with 0.05% toluidine blue O for 10 minutes and washed. A few seconds after CUENE addition, the samples were examined under the microscope. Micrographs had to be taken immediately, since the entire sample swelled at longer times.

The results are shown in Fig. 2. It can be seen that the swelling occurs in the middle of fibers and at kinks, both of which represent localized compression damage. In addition, blunt fiber tips, which have been cut, also swell, whereas tapered tips do not generally show swelling. Since fiber length distribution did not change upon fiberization, the blunt tips are most likely due to chipping rather

than fiberization. This technique cannot be used quantitatively, due to the irreproducibly short reaction times with CUENE. However, qualitative information is obtained, since those sites which swelled with CUENE probably serve as points for attack by oxygen/alkali as well.

Compression Rolled (Hosmer) Chips

Loblolly pine chips were soaked in a 5% solution of sodium carbonate at 10% consistency at room temperature for 1 hour and then steamed for 15 min at 15 psig. They were placed in a hopper and fed to the rollers by means of a rapidly moving conveyor intended to feed one chip at a time. The steel rollers were 24 inches in diameter and 6 inches wide and were set for a clearance of 0.030 inch (ca. 0.8 mm). The rollers rotated in opposite directions, so that both were feeding into the nip. The yield was 96.2%. This treatment is similar to that used previously by others (2), except the rolls were not embossed. The product was similar in appearance to the published pictures, except the chips were not extended to the same degree. Interestingly, the equipment was designed for compression debarking of whole tree chips, and results on that application using larger rollers have recently been published (3).

Flakes

Loblolly pine logs were peeled with a drawknife to remove bark, and then cut into 1/2 inch lengths. These were pushed into a rotating cutter blade which cut them 1/2 inch wide and 0.045 inch (ca. 1.1 mm) thick, with the grain. This produced a very uniform product, with a small amount of fines which was screened out.

PULPING STUDIES

All OA pulping reported here was carried out at low consistency under conditions of high oxygen availability (1). Cooking conditions are given in the tables. Kraft reference pulps were prepared in the laboratory as described previously (1).

Uniformity of Reaction

As mentioned earlier, one of the major problems in oxygen pulping is getting a uniform reaction. This is particularly true with starting material which has not been fiberized. Nonuniform pulping shows up as a large amount of rejects. Table I shows the results of cooking the nonfiberized wood samples. The kappa numbers are given for the accepts only; the rejects had higher kappa numbers. It can be seen that until the kappa number gets below about 40, the rejects levels are quite high. The flakes gave the best results, becoming almost reject-free at kappa number 39. Unfortunately, this took 6.5 hours at the reaction temperature studied. The time can be shortened by increasing the temperature, but a point is reached where uniformity becomes more of a problem. The Hosmer chips were considerably better than the conventional chips, giving about one-third as many rejects. Conventional chips (nominally 5/8 inch) were considered to be unacceptable under these conditions. This is in contrast to the results found with red maple (1).

Strength Properties

Strength properties were obtained on a number of OA pulps, and these are compared with kraft pulps from chips in Table II. The OA pulps on nonfiberized material were listed in Table I, and they can be identified by the yield. The cooking conditions for the other OA pulps are given in footnotes in Table II. All values are given for 0.600 sheet density.

The first thing to note is that the yields were better starting with nonfiberized wood. The yields from the fiberized samples are overall yields from the two-stage process. The first-stage yields were simulated in the laboratory, and thus have a larger uncertainty associated with them. Nevertheless, the differences are large enough to be considered real. Also, the sample which was fiberized in sodium carbonate/bicarbonate (A-3) gave a higher yield than the one fiberized in sodium hydroxide (A-2). These yield results suggest that having

oxygen present right from the beginning of an OA pulping process helps preserve hemicelluloses in the final pulp. This can be explained by an oxidative stopping reaction (4).

The strength properties of the OA pulps did not match those of the kraft reference pulps. Furthermore, when the same starting material was taken from high to low kappa number by OA pulping, the strength properties tended to go down rather than up, except for tear. This is in contrast to the kraft pulps, where all strength properties were better at the lower kappa number. The flakes gave the best strength properties for the OA pulps, although the Hosmer chips gave virtually identical properties in the low-kappa range.

Strength Properties of Kraft Pulps from Several Starting Materials

In order to determine how much of the strength differences between oxygen and kraft pulps was due to the different starting materials and how much was due to the OA chemistry, it is necessary to make the comparisons on the same starting materials.

Table III gives strength properties for kraft pulps prepared from the various starting materials described above. The kraft pulps from chips are also included again in this table for convenient comparison. It can be noted that the kraft pulps from chips were strongest, and that all other starting materials gave weaker pulps. Thus, all of the methods of preparing material suitable for oxygen pulping result in less strength. If it were possible to pulp loblolly pine chips with oxygen/alkali, stronger pulps could be expected.

In comparing oxygen pulps with kraft pulps from the same starting materials, it can be seen that the kraft pulps are stronger. Part of this difference can be explained by the higher yields, which give fewer fibers in the oxygen pulp handsheets. However, particularly in the case of tear strength, the oxygen process gives inherently weaker pulps.

CONCLUSIONS

Fiberization of loblolly pine before oxygen pulping introduces mechanical damage to the fibers which results in a strength loss. The damage does not shorten the fibers, but appears to be compression damage. Localized chemical degradation could occur in oxygen pulping of such fiberized samples. Oxygen pulping of thin flakes or compression rolled chips can produce stronger pulps in higher yields with acceptable rejects levels. However, longer reaction times are required. Conventional chips of loblolly pine cannot be used under these conditions to produce pulps in acceptable yields and rejects levels. Strengths of all the oxygen pulps are below those of kraft. A large portion of these strength differences is due to preparation of the wood for OA pulping, but a substantial portion is still due to the OA pulping stage itself. Thus, improvements are needed in both areas before these pulps are attractive for commercial use.

ACKNOWLEDGMENTS

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TABLE I. Results of Cooking Nonfiberized Samples[a,b]

Starting material	Chips	Chips	Flakes	Flakes	Hosmer
Temperature, °C	130	130	130	130	130
Time to temp., min	30	30	30	30	10
Time at temp., min	300	450	240	390	450
Yield (kappa)[b]	76.0(73)	61.0(43)	65.1(70)	58.9(39)	59.5(41)
Rejects, %	58.5	21.0	16.1	0.5	7.6

[a]All oxygen cooks in this report at 2550 psi; 9.9 g/liter Na_2CO_3, 7.6 g/liter $NaHCO_3$, 1.5% consistency.

[b]Yields include rejects; kappas on accepts.

TABLE II. Strength Properties of OA and Kraft Pulps[a,b]

	High Kappa Number Range			
Type	OA[c]	OA[d,e]	OA	kraft
Starting material	A-2	A-3	flakes	chips
Yield (kappa)	58.7(89)	64.1(86)[b]	65.1(70)	51.7(78)
Freeness	505	270	505	445
Breaking length, km	8.0	8.5	9.5	11.0
Burst factor	58	55	60	85
Tear factor	85	65	77	123
Zero span, km	13.9	12.4	15.5	19.8

	Low Kappa Number Range				
Type	OA[f]	OA[e]	OA	OA	kraft
Starting material	A-3	Hosmer	chips	flakes	chips
Yield (kappa)	52.6(39)	59.6(41)	61.0(43)	58.9(39)	46.9(33)
Freeness	640	650	410	600	300
Breaking length, km	7.3	7.8	8.4	7.9	11.6
Burst factor	50	47	53	46	90
Tear factor	88	86	72	88	133
Zero span, km	14.0	15.8	15.6	15.4	22.3

[a] Strength values interpolated to 0.600 sheet density, unless noted.
[b] Kappa and strength values after removal of rejects.
[c] Cooked 2.0 hr at 130°C.
[d] Cooked 3.3 hr at 130°C.
[e] Strength values extrapolated to 0.600 sheet density.
[f] Cooked 6.0 hr at 130°C.

TABLE III. Strength Properties of Kraft Pulps[a]

High Kappa Number Range				
Starting material	A-2[b]	Hosmer	flakes	chips
Yield (kappa)	52.7(82)	51.6(73)	52.0(69)	51.7(78)
Freeness	170	610	550	445
Breaking length, km	9.2	9.3	9.7	11.0
Burst factor	66	66	72	85
Tear factor	101	126	138	123
Zero span B.L., km	16.6	19.9	20.5	19.8

Low Kappa Number Range				
Starting material	A-2	A-3	Hosmer	chips
Yield (kappa)	47.2(40)	44.8(40)	47.3(29)	46.9(33)
Freeness	550	530	480	300
Breaking length, km	8.3	8.1	8.5	11.6
Burst factor	63	61	60	90
Tear factor	113	120	141	133
Zero span B.L., km	15.6	15.1	19.2	22.3

[a]All values for 0.600 sheet density.
[b]Extrapolated strength and freeness values, all others interpolated.

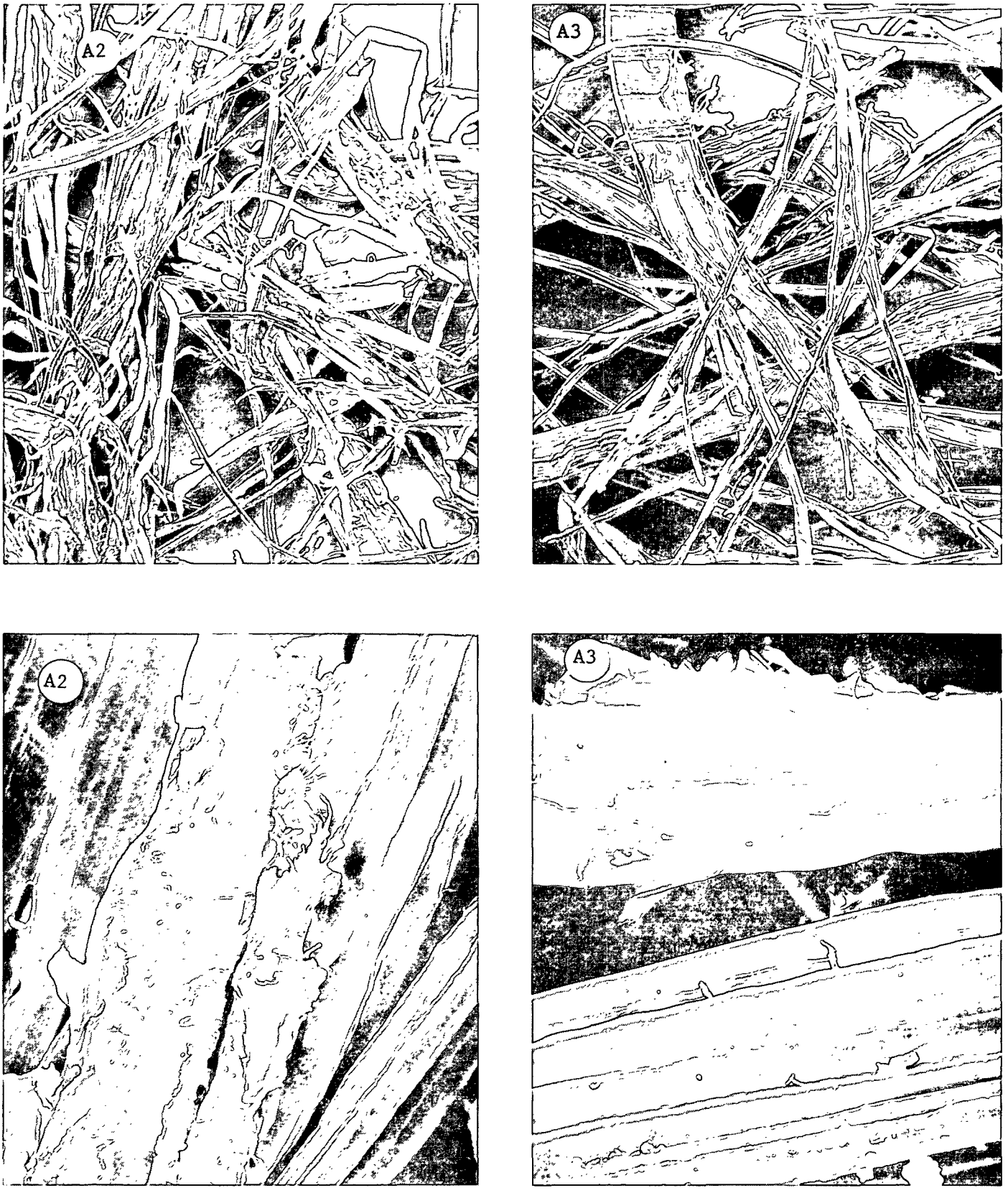

Figure 1. Scanning electron micrographs of fiberized wood, 50X and 500X magnification

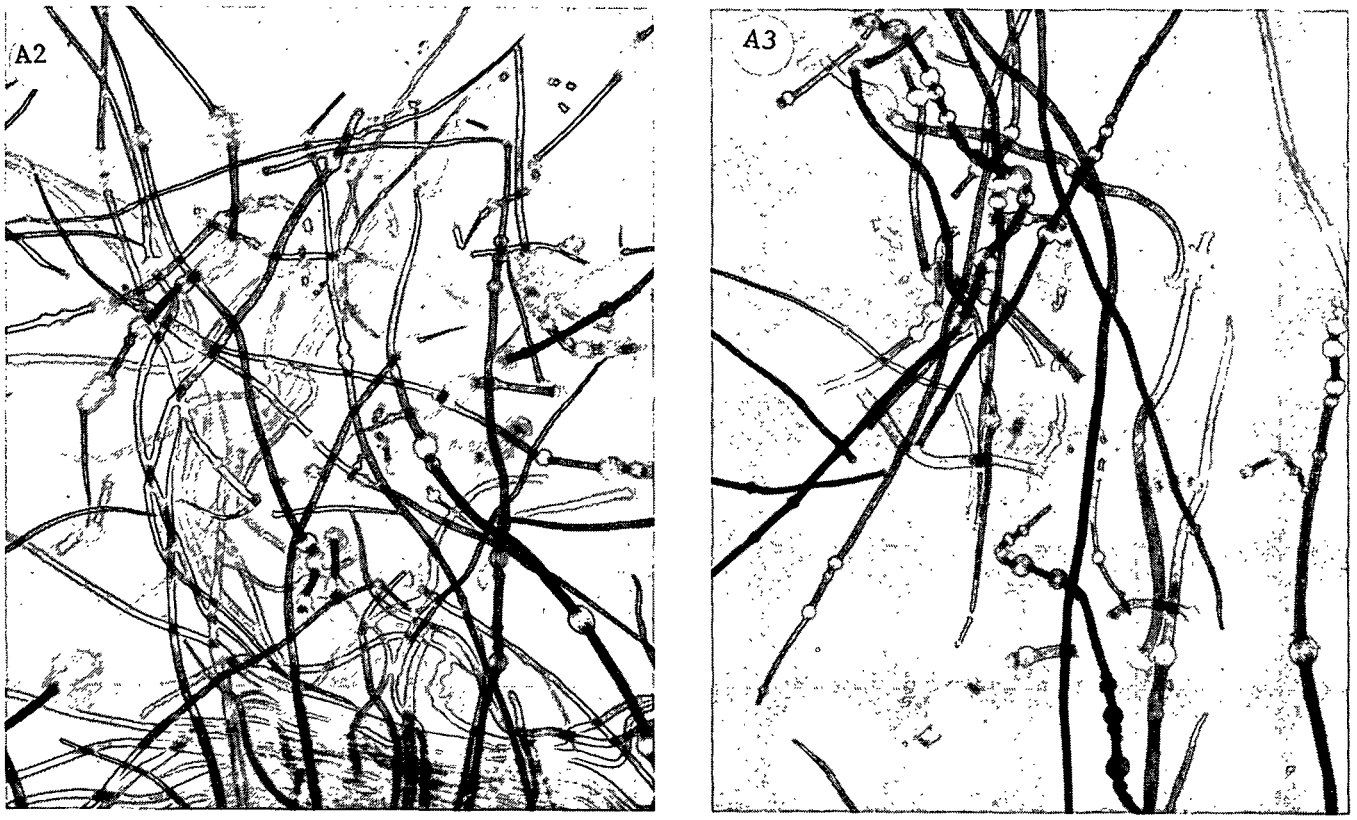

Figure 2. Light micrographs of CUENE swollen fibers, 30X magnification